RHEOLOGICAL AND STRUCTURAL CHARACTERIZATION OF AN AR MESOPHASE PITCH

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Introduction

During melt spinning of carbon fibers, mesophase pitch is extruded through fine capillaries and stretched during fiber winding. This results in a complex flow process involving shear and elongational deformations. Modeling the flow of this system is made more difficult by the coupled fluid-structure interaction and the non-Newtonian viscoelastic behavior of mesophase pitch. Previously, rheological characterization of mesophase pitch was incomplete due to the difficulty of measuring the first normal stress difference, N_1, and extensional viscosity, η_e [1]. In this work both N_1 and η_e was measured for an AR mesophase pitch. These measurements will aid in selecting an appropriate constitutive equation.

Several constitutive models have been derived for the flow of liquid crystals [2,3]. A scaling argument, proposed by Marrucci, has been successfully used to describe the size of the poly-domain structure during flow for an AR mesophase pitch [4]. In this work the size of the poly-domain structure is measured at different rates of shear and rest times.

Experimental

The material characterized during this study was a synthetic, naphthalene-based mesophase pitch, produced by Mitsubishi Gas Chemical Company. This mesophase was manufactured to minimize the volatile content noted in previous AR mesophase. Solid discs of mesophase pitch were created by grinding the mesophase into a fine powder and then placing the powder into a vacuum pelletizer. Vacuum pelletized samples were prepared for both rheological testing and structural analysis.

Rheological experiments were carried out using a Rheometrics ARES controlled-strain rotational rheometer and an ACER capillary viscometer. Steady shear experiments were carried out on the ARES using 50mm cone and plate fixtures with a 0.04 radian cone angle. During sample loading, solid discs of mesophase were squeezed at the test temperature and then allowed to relax until the normal and torque stresses were approximately zero. All tests were started from this stress-free state. Shear rates of 0.01 to $10s^{-1}$ were studied at temperatures ranging from 305 to 325^{o}C.

Shear viscosity and extensional viscosity measurements were obtained using the ACER capillary viscometer. Shear viscosity measurements were made using a cylindrical capillary die with diameter of 1mm and length of 30mm. Extensional viscosity measurements were made using a hyperbolic capillary die [5] with an inlet diameter of 19.96mm, an outlet diameter of 0.603mm, and a length of 25mm.

Structural experiments were conducted using a Rheometrics RDS-II controlled-strain rotational rheometer. Sheared samples were collected from the 25mm cone-and-plate geometry and analyzed using a polarized light microscope.

Results and Discussion

The steady shear viscosity, shown in figure 1, exhibits the typical trend seen for low molecular weight liquid crystals [6]. At low shear rates, below $1s^{-1}$, the mesophase is shear thinning with a slope of -1/2, then a plateau region is reached. As was previously reported for this mesophase [1], there is a "kink" in the shear viscosity curve during the transition from shear thinning to the plateau viscosity. This behavior has also been reported for some liquid crystal polymers [7-9]. In figure 2 we see that the first normal stress difference exhibits a negative value at low shear rates and becomes positive at higher shear rates. Negative values of N_1 have also been observed for some liquid crystal polymers. A model of poly-domain flow [10] predicts the presence of a kink in the shear viscosity curve as the first normal stress difference changes from negative to positive values. These predictions are for molecules that tumble and oscillate at low rates of shear and become stable at high rates of shear.

In figure 3 it can be seen that the shear viscosity, at higher shear rates, undergoes a transition from a constant viscosity to shear thinning. This behavior is consistent with the observations of Onogi and Asada [6]. However, viscous dissipation effects often dominate at these high shear rates. Therefore, the validity of these shear viscosity values will be further investigated. At the time of this writing, measured values of the extensional viscosity have not been obtained. Extensional viscosity data will be presented at the conference.

Sheared samples of mesophase have been collected and examined under polarized light. Figure 4 shows a sample of mesophase pitch subjected to a shear rate of $0.2s^{-1}$. More cross sections over a wider range of shear rates will be presented at the conference.

Conclusions

A more complete rheological characterization of mesophase pitch has been accomplished. The shear viscosity follows the trend reported by Onogi and Asada and the kink corresponds with negative first normal stress differences as proposed by Marrucci and Maffettone.

References

1. Cato AD, Edie D. Normal force rheological measurements for an AR mesophase pitch. Extended abstracts, Eurocarbon 2000 Berlin (Berlin, Germany): European Carbon Association, 2000; 15-16.
2. Marrucci G, Maffettone PL. Description of the liquid-crystalline phase of rodlike polymers at high shear rates. Macromolecules 1989;22:4076-4082.
3. Singh AP, Rey AD. Microstructure constitutive equation for discotic nematic liquid crystalline materials. Part 1: Selection procedure and shear flow predictions. Rheol Acta 1998;37:30-45.
4. Fleurot O, Edie DD. Modeling of structure development during flow of mesophase pitch through capillaries. Extended abstracts, 23rd biennial conf. on carbon Penn State (Pennsylvania. USA): American Carbon Society, 1997; 416-417.
5. Collier JR, Romanoschi O, Petrovan S. Elongational rheology of polymer melts and solutions. J. of Appl. Poly. Sci. 1998;69:2357-2367.
6. Onogi S, Asada T. Rheology and rheo-optics of polymer liquid crystals. Rheology 1980;1:127-146.
7. Grizzuti N, Cavella S, Cicarelli P. Transient and steady-state rheology of a liquid crystalline hydroxypropylcellulose solution. J. Rheol. 1990;34:1293-1310.
8. Berry GC. Rheological properties of nematic solutions of rodlike polymers. Mol. Cryst. Liq. Cryst. 1988;165:333-360.
9. Kiss G, Porter RS. Rheology of concentrated solutions of helical polypeptides. J. Polym. Sci. Phys. Ed. 1980;18:361-388.
10. Marrucci G, Maffettone PL. Nematic phase of rodlike polymers. II. Polydomain predictions in the tumbling regime. J. Rheol. 1990;34(8):1231-1244.

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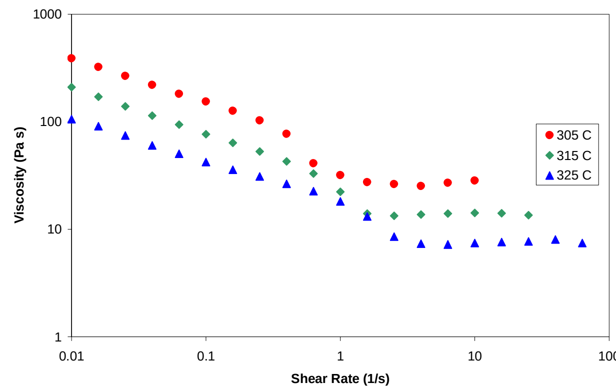

Figure 1. Steady shear viscosity of mesophase pitch.

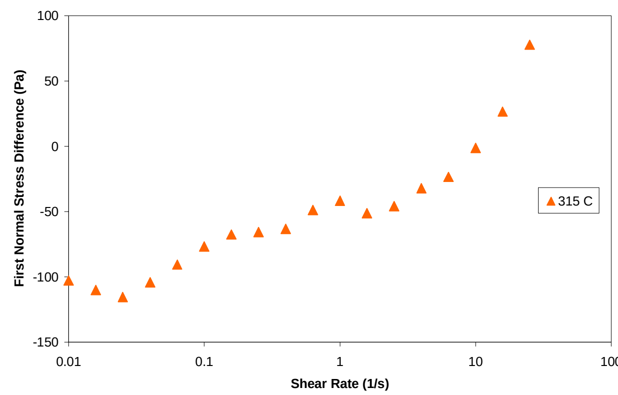

Figure 2. First normal stress difference at 315 ^{o}C.

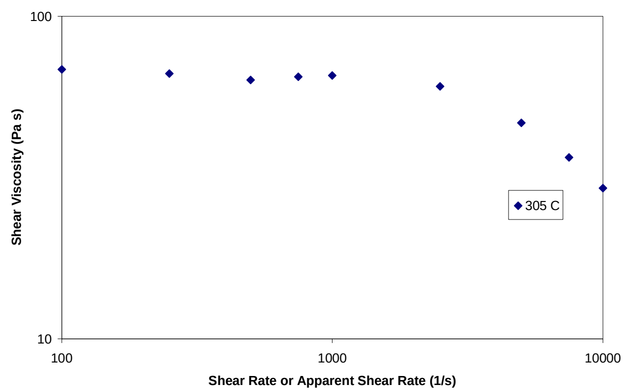

Figure 3. High shear viscosity at 305 ^{o}C.

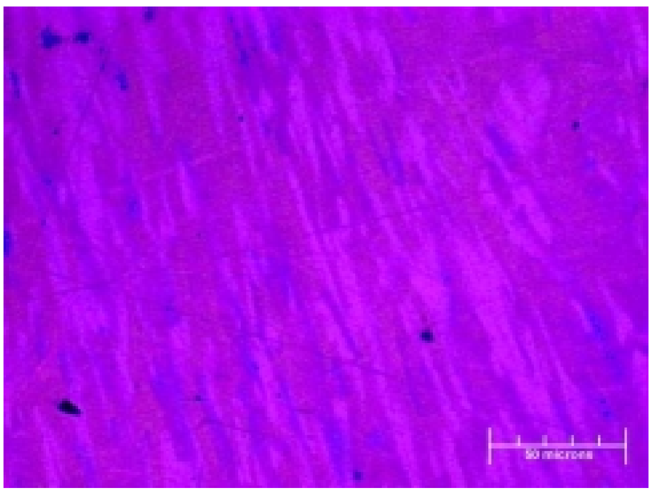

Figure 4. Sheared mesophase in the flow/vorticity plane.